

# Studies on Thermal and Morphological Behavior of Siliconized Epoxy Bismaleimide Matrices

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**ABSTRACT:** Novel bismaleimide-modified siliconized epoxy intercrosslinked network systems were developed. Siliconized epoxy systems containing 5, 10, and 15% siloxane units were prepared using epoxy resin and hydroxyl-terminated polydimethylsiloxane (HTPDMS) with  $\gamma$ -aminopropyltriethoxysilane ( $\gamma$ -APS) as a compatibilizer and dibutyltindilaurate as a catalyst. The siliconized epoxy systems were further modified with 5, 10, and 15% (wt %) of bismaleimide [(N,N'-bismaleimido-4,4'-diphenylmethane) (BMI)] and cured by diaminodiphenylmethane (DDM). Differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and heat-distortion temperature measurement of the matrix samples were carried out to assess their thermal behavior. DSC thermograms of the BMI-modified epoxy systems show unimodal reaction exotherms. The glass transition temperature ( $T_g$ ) of the cured BMI-modified epoxy and siliconized epoxy systems increases with increasing BMI content. Thermogravimetric analysis and heat-distortion temperature measurements indicate that the thermal degradation temperature and heat-distortion temperature of the BMI-modified epoxy and siliconized epoxy systems increase with increasing BMI content. The morphology of the BMI-modified siliconized epoxy systems was also studied by scanning electron microscopy (SEM). © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 2330–2346, 2001

**Key words:**  $\gamma$ -APS; dibutyltindilaurate; diaminodiphenylmethane; siliconized epoxy resin; BMI-modified siliconized epoxy resin; glass transition temperature; thermal stability; heat-distortion temperature; SEM micrograph

## INTRODUCTION

The development of modern technology lays emphasis on reliable high-performance composite materials having light weight with excellent thermal and mechanical properties for applications such as a vacuum (space) or strong electric, magnetic, or irradiation fields under adverse environ-

mental conditions.<sup>1</sup> Epoxy resin-based composites are widely used as laminates for printed circuit boards, aerospace, ballistic, and engineering hardware components, pollution-control equipment, automotive parts, electrical components and rehabilitation products, etc., because of their excellent bonding, thermal, and mechanical characteristics.<sup>2–7</sup>

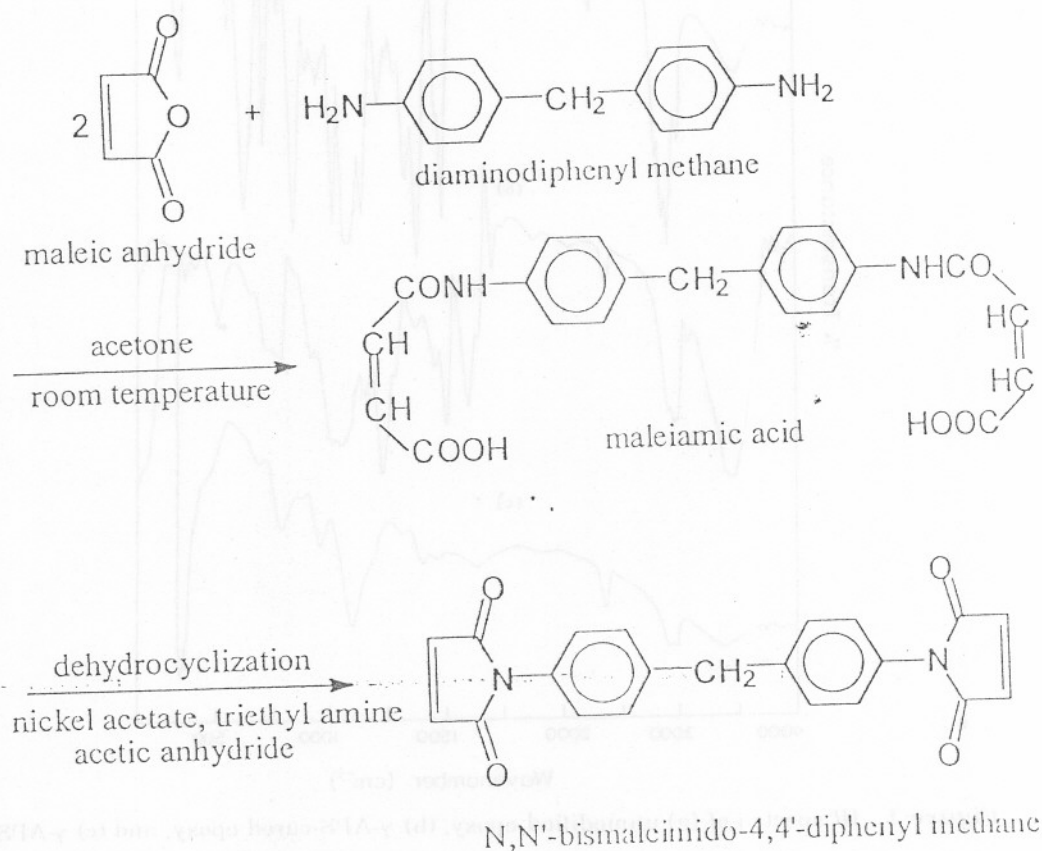
However, the mechanical and thermal characteristics of epoxy matrices are not sufficient to meet the requirements of high-performance structural products. To enhance toughness and thermal stability in order to make it suitable for high-performance aerospace and engineering ap-

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Scheme 2. Synthesis of BMI.

ysilane ( $\gamma$  APS) as a compatibilizer, dibutyltin dilaurate as a catalyst, and bismaleimide.

## EXPERIMENTAL

### Materials

Epoxy resin (diglycidyl ether of bisphenol A, DGEBA) LY556, having an epoxy equivalent of about 180–190 and viscosity of about 10,000 cP, and 4,4-diaminodiphenylmethane (DDM) were obtained from Ciba-Geigy Ltd. (Mumbai, India). Bismaleimide [*N,N'*-bismaleimido-4,4'-diphenylmethane (BMI)] and HTPDMS having a molecular weight of 17,000–18,000 and a viscosity of 800–900 cP were prepared by the reported procedure.<sup>25</sup> The HTPDMS used in the present study was synthesized from octamethylcyclotetrasiloxane by the ring-opening polymerization technique. The compatibilizer  $\gamma$ -APS and the dibutyltin dilaurate catalyst were obtained from Union Carbide (Houston, TX) and Merck (Darmstadt, Germany), respectively.

### Preparation of Siliconized Epoxy Prepolymer

A fixed amount of epoxy resin, a varying amount of HTPDMS, a stoichiometric amount of  $\gamma$ -APS (with respect to the ethoxy group), and the dibutyltin dilaurate catalyst (Table I) were thoroughly mixed at 90°C for 10 min under constant stirring. The product was then degassed to remove ethanol formed during the condensation reaction between  $\gamma$ -APS and HTPDMS (Scheme 1).

### Preparation of BMI

BMI was prepared according to the reported procedure.<sup>25</sup> The reaction scheme is given in Scheme 2.

### Preparation of Siliconized Epoxy BMI Blend

The stoichiometric amount of DDM was dissolved into siliconized epoxy resin at 90°C under vigorous stirring. After complete dissolution, a calculated amount of BMI was added. The agitation was continued at 100°C until a homogeneous product was obtained. The product was subjected

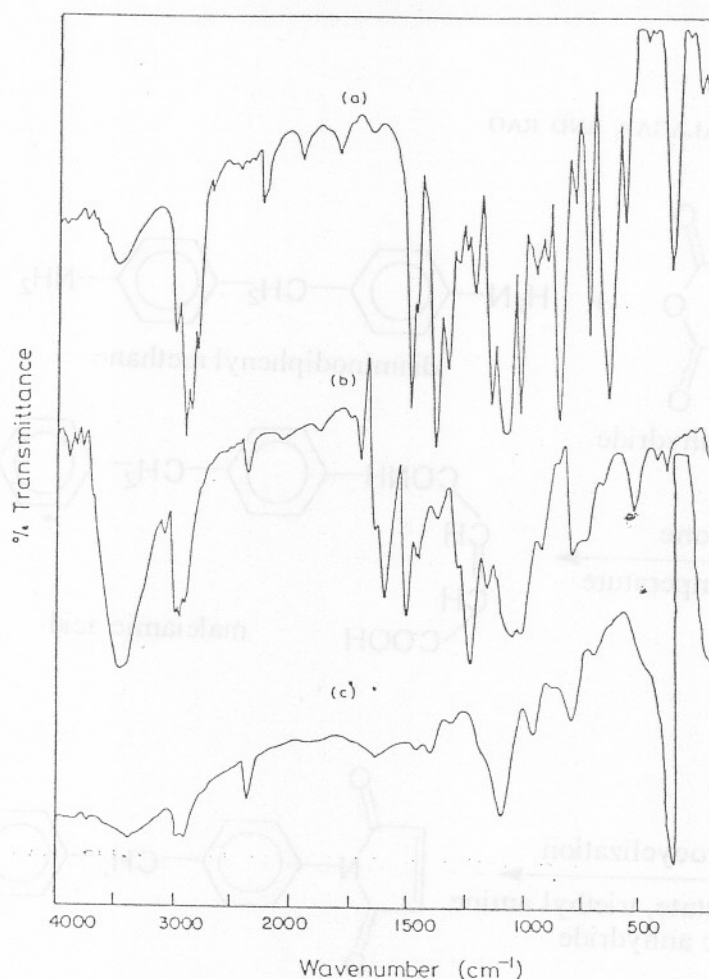


Figure 1 IR spectra of (a) unmodified epoxy, (b)  $\gamma$ -APS-cured epoxy, and (c)  $\gamma$ -APS.

to vacuum treatment to remove the trapped air and then cast and cured at 120°C for 1 h. The castings were then postcured at 180°C for 2 h and finally removed from the mold and characterized.

#### Test Methods

The IR spectra were recorded on a Perkin-Elmer 781 infrared spectrometer and the spectra are presented in Figures 1 and 2. The glass transition temperature ( $T_g$ ) of the samples was determined using DSC 2910 (TA instruments USA) in the temperature range between 50 and 250°C at a heating rate of 10°C min<sup>-1</sup>. Thermogravimetric analysis (TGA) was carried out using Thermal Analyst 2000 (TA Instruments, USA) at a heating rate of 10°C min<sup>-1</sup> in an inert atmosphere.

Fractured surfaces were obtained from plain strain fracture toughness tested specimens using an Instron testing machine (Model 6025, UK) at a crosshead speed of 2 mm/min. Excess material

was removed from the other faces of the specimens by a razor blade. The fracture surfaces of the specimens were coated with gold and examined under a scanning electron microscope (SEM; Leica Cambridge, Stereoscan Model 440).

## RESULTS AND DISCUSSION

### Spectral Analysis

The formation of siliconized epoxy network structure proceeds in two steps and was evaluated by IR (Fig. 1): The first step involves the reaction between the epoxide ring of the epoxy resin and the amino group of the  $\gamma$ -APS and was confirmed by the disappearance of the epoxy band at 913 cm<sup>-1</sup> and the appearance of the hydroxyl band at 3420 cm<sup>-1</sup>. Absorption peaks appeared at 2980 and 2850 cm<sup>-1</sup> and 1370 cm<sup>-1</sup>, confirming the presence of  $\text{—Si—O—CH}_2\text{CH}_3$  and  $\text{—Si—}$



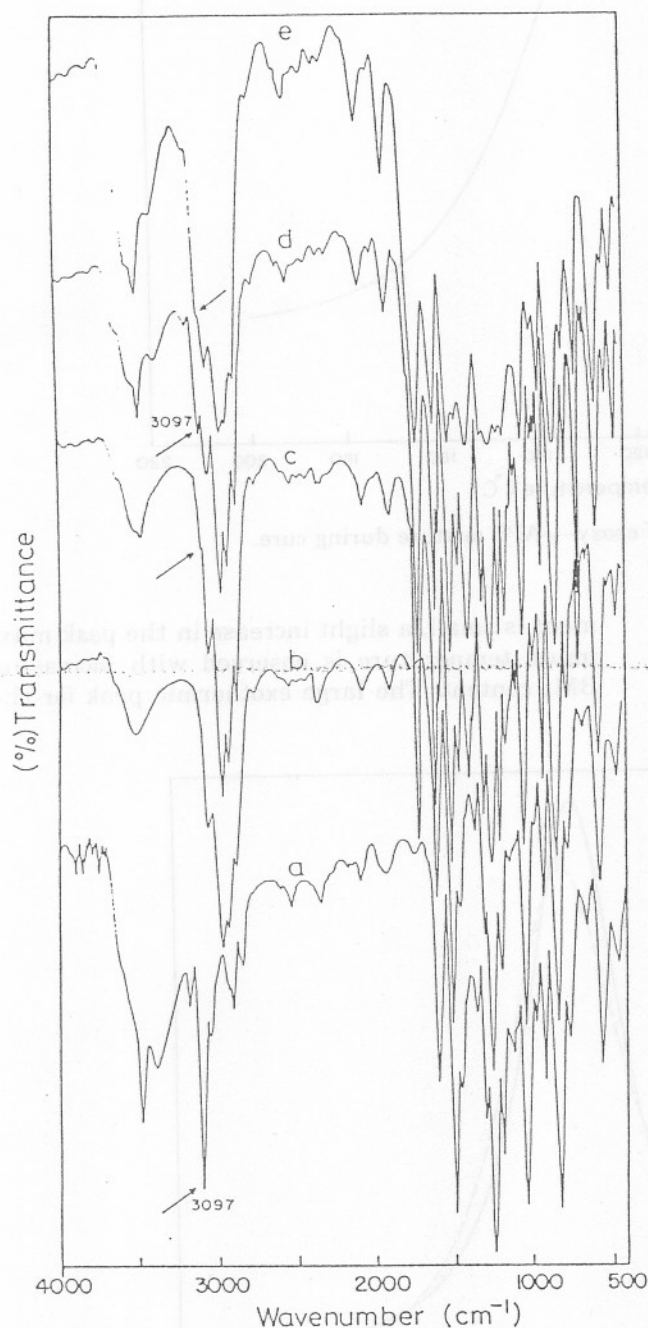


Figure 2 IR spectra of (a) pure BMI, (b) unmodified epoxy, (c) epoxy/BMI: 100/10, (d) epoxy/BMI: 100/50, and (e) epoxy/BMI: 100/50 after heating 130°C for 3 h.

(CH<sub>2</sub>)<sub>3</sub>—, respectively. In the second step, the alkoxy groups present in  $\gamma$ -APS react with the hydroxyl groups of HTPDMS.

Figure 2(a,b) represents IR spectra of pure BMI and unmodified epoxy, respectively. The peak at 3097 cm<sup>-1</sup> in Figure 2(a) is due to H—C= vibration and is widely accepted as a reference to follow the conversion of BMI double bonds.

IR spectra for the mixture of epoxy and BMI of varying composition are presented in Figure 2(c) (epoxy/BMI: 100/10) and 2(d) (epoxy/BMI: 100/50). The occurrence of the peak at 3098 cm<sup>-1</sup> in Figure 2(d) confirms the presence of BMI double bonds in the epoxy mixture, whereas the peak is poorly resolved in Figure 2(c) due to a lower concentration of BMI.

The IR spectrum of Figure 2(e) (epoxy/BMI: 100/50) taken after heating the mixture at 130°C for 3 h indicates the decrease in the intensity of the H—C= vibration peak at 3097 cm<sup>-1</sup>. This confirms the occurrence of homopolymerization of BMI in the presence of epoxy resin at a lower temperature, whereas the homopolymerization of pure BMI normally occurs at 180°C (Fig. 6). Hence, epoxy resin aids the homopolymerization of BMI at lower temperature.

#### Cure Reaction Behavior

The HTPDMS modification of epoxy resin proceeds in two steps: The first step involves the reaction between —NH<sub>2</sub> groups of  $\gamma$ -APS and oxirane rings of the epoxy resin. From the DSC thermogram (Fig. 3), it is evident that the reaction starts at 100°C and reaches its peak maximum at 120°C. Further, the reaction between —OCH<sub>2</sub>CH<sub>3</sub> groups of  $\gamma$ -APS and the hydroxyl groups of HTPDMS also occurs simultaneously and is accelerated during the degassing process. In the second step, the —NH<sub>2</sub> groups of DDM react with the remaining oxirane rings of the epoxy resin. The epoxy-DDM reaction starts at 120°C and reaches its peak maximum at 167°C (Fig. 4). The large exotherm obtained for the epoxy-DDM system is due to the following reactions: (i) oxirane ring-opening reaction with active amine hydrogens of DDM and (ii) autocatalytic reaction of the oxirane ring with pendent hydroxyl groups of epoxy resin and hydroxyl groups formed during reaction (i) (Fig. 5). The exotherm obtained for the reaction of epoxy resin with a mixture of  $\gamma$ -APS and DDM shows unimodal behavior (Fig. 4). The exotherm starts at 70°C and reaches its peak maximum at 165°C, suggesting that the reaction proceeds in a homogeneous path.

DSC thermograms of the BMI-modified epoxy resin containing 5, 10, and 15% BMI-incorporated epoxy systems are presented in Figure 6. BMI-incorporated epoxy systems show unimodal reaction exotherm due to its lower concentration. In the BMI-incorporated systems, the reaction com-

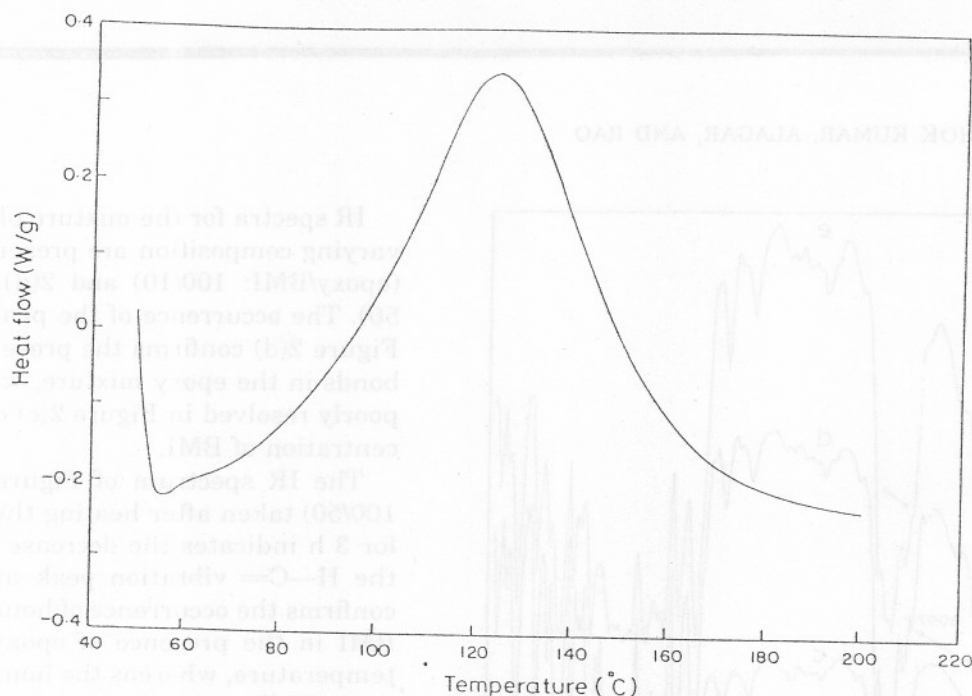


Figure 3 DSC thermogram of epoxy- $\gamma$ -APS mixture during cure.

mences at 120°C and reaches the peak maximum at 169, 172, and 175°C for 5, 10, and 15% respectively. Since, the concentration of the BMI incre-

ment is small, a slight increase in the peak maximum temperature is observed with increasing BMI content. The large exothermic peak for the

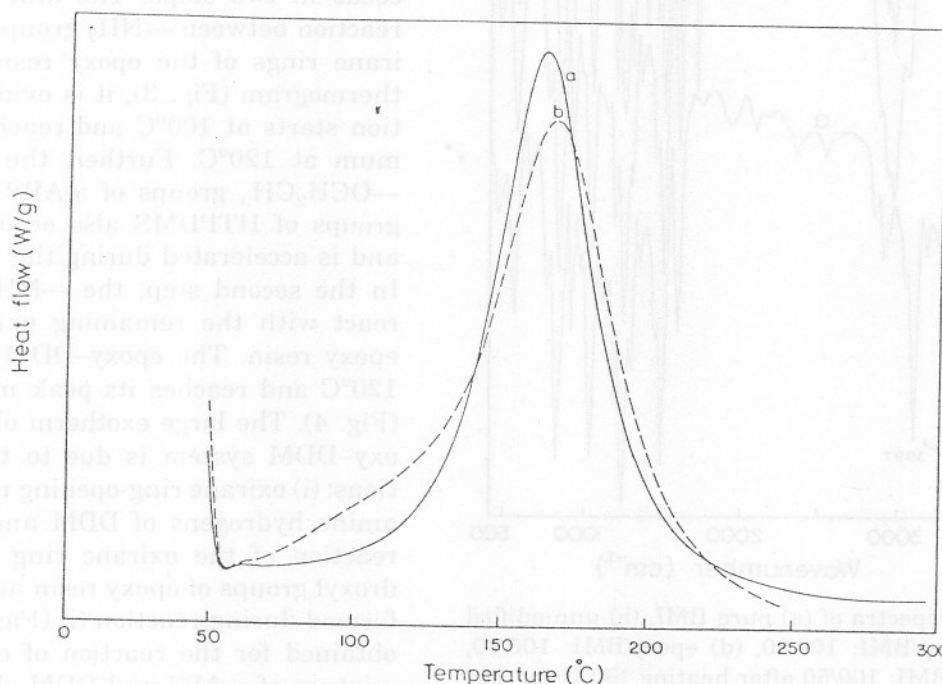


Figure 4 DSC thermograms of (a) epoxy-DDM and (b) mixture of epoxy-DDM- $\gamma$ -APS systems during cure.

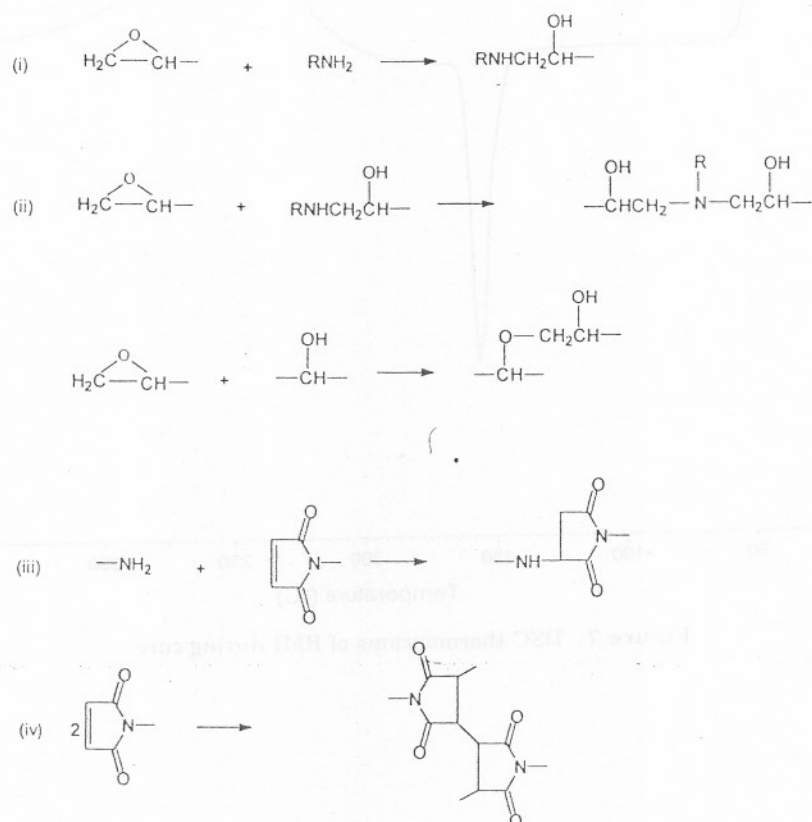


Figure 5 Reactions involved during the curing process of BMI-modified epoxy systems.

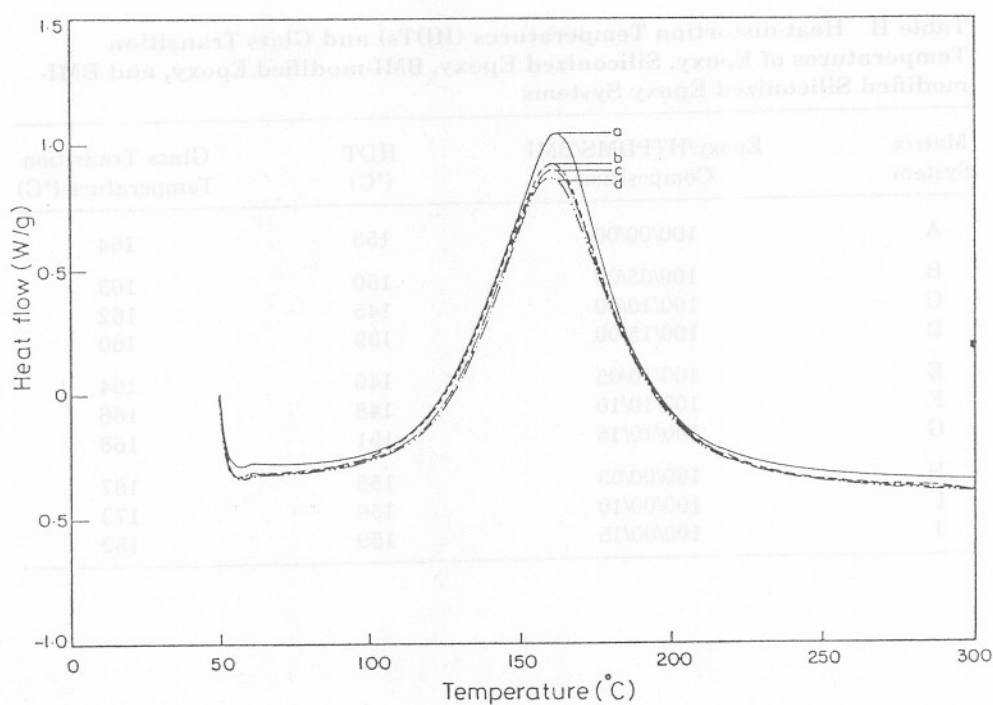


Figure 6 DSC thermograms of epoxy-BMI systems during cure: (a) epoxy-DDM; (b) epoxy-DDM-5% BMI; (c) epoxy-DDM-10% BMI; (d) epoxy-DDM-15% BMI.

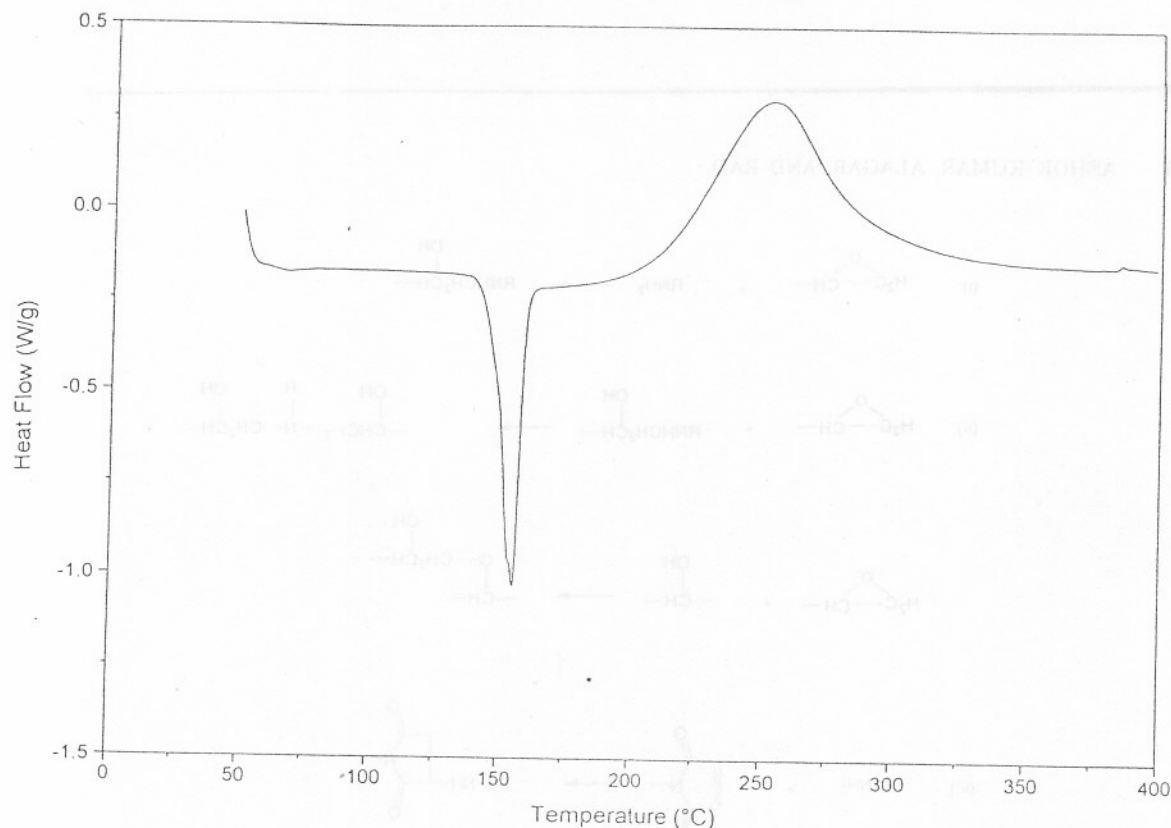


Figure 7 DSC thermograms of BMI during cure.

Table II Heat-distortion Temperatures (HDTs) and Glass Transition Temperatures of Epoxy, Siliconized Epoxy, BMI-modified Epoxy, and BMI-modified Siliconized Epoxy Systems

Matrix System	Epoxy/HTPDMS/BMI Composition	HDT (°C)	Glass Transition Temperature (°C)
A	100/00/00	153	164
B	100/05/00	150	163
C	100/10/00	145	162
D	100/15/00	139	160
E	100/10/05	146	164
F	100/10/10	148	166
G	100/10/15	151	168
H	100/00/05	155	167
I	100/00/10	156	173
J	100/00/15	159	182



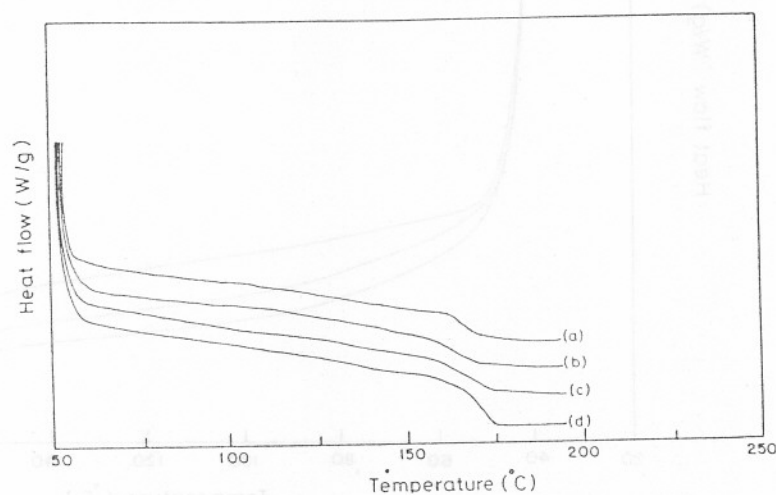


Figure 8 DSC traces of epoxy and siliconized epoxy systems: (a) unmodified epoxy and (b) 5%, (c) 10%, and (d) 15% HTPDMS-modified epoxy systems.

BMI-incorporated system is due to the following reactions: (iii) addition reaction of  $\text{—NH}_2$  groups of DDM with double bonds of BMI (Michael addition) and (iv) BMI homopolymerization reaction in addition to reactions (i) and (ii) (Fig. 5). It is observed that the homopolymerization of the BMI reaction starts at  $180^\circ\text{C}$  (Fig. 7). Earlier, it was

reported that reaction (iv) is the least possible due to the requirement of higher activation energy to initiate the homopolymerization of BMI. However, according to Musto et al.,<sup>22</sup> in the presence of epoxy resin, the same reaction (homopolymerization of BMI) starts at about  $120\text{--}140^\circ\text{C}$ , because of the formation of zwitterion adduct be-

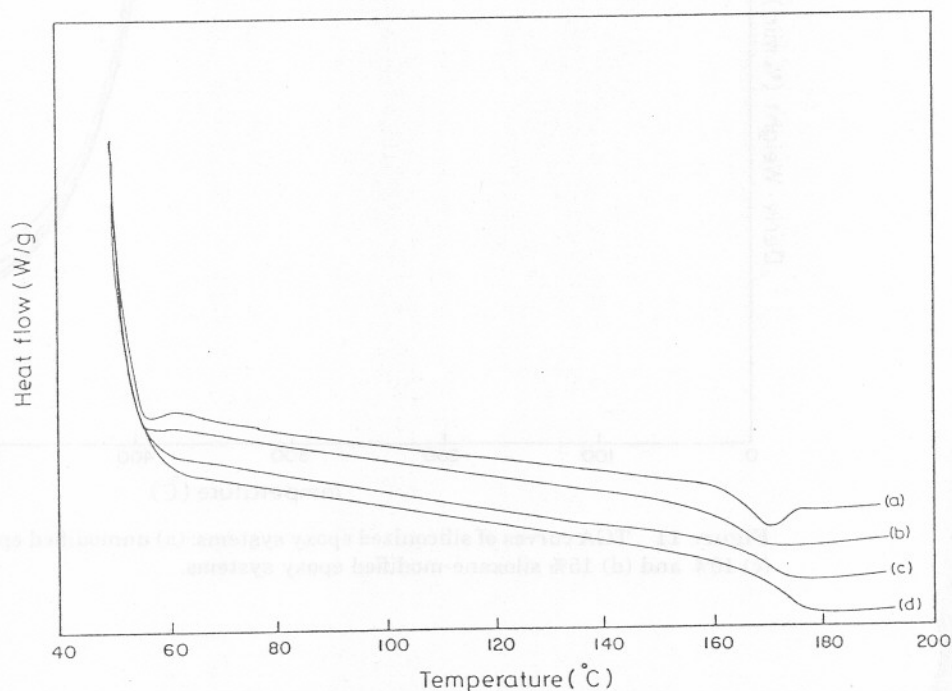


Figure 9 DSC traces of BMI-modified epoxy systems: (a) unmodified epoxy and (b) 5%, (c) 10% and (d) 15% BMI-modified epoxy systems

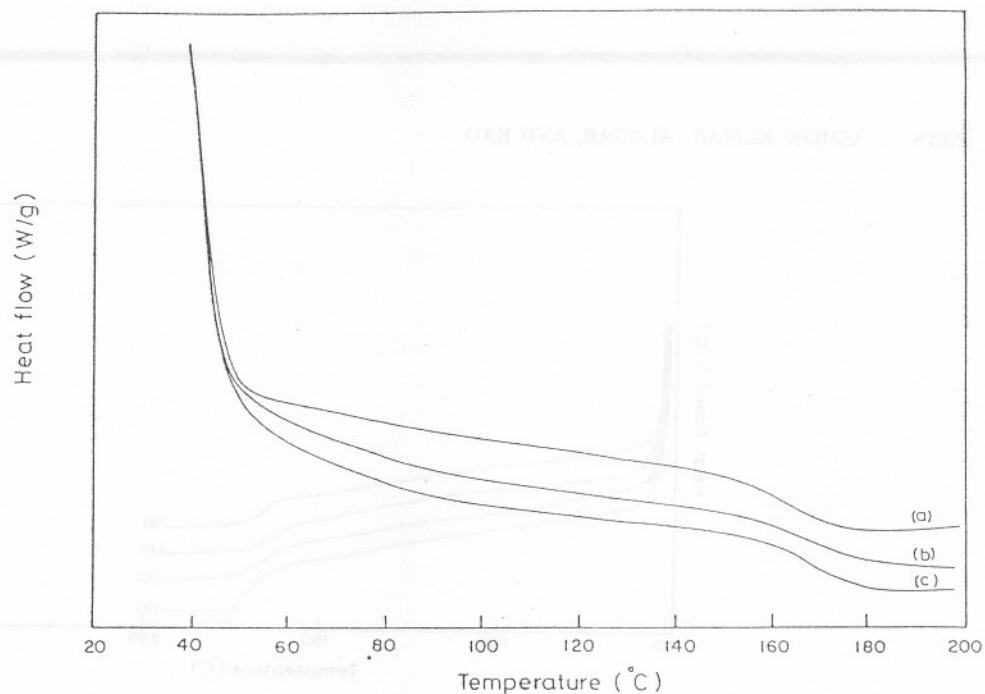


Figure 10 DSC traces of 10% siliconized epoxy/BMI systems: (a) 5%, (b) 10%, and (c) 15% BMI-modified 10% siliconized epoxy systems.

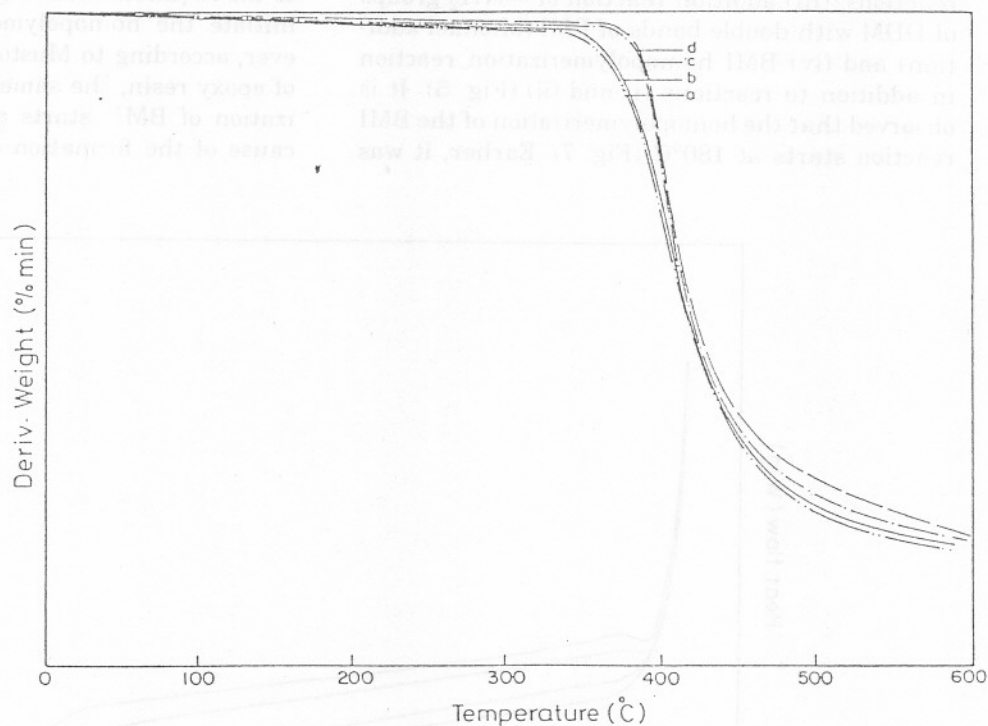


Figure 11 TGA curves of siliconized epoxy systems: (a) unmodified epoxy, and (b) 5%, (c) 10% and (d) 15% siloxane-modified epoxy systems.

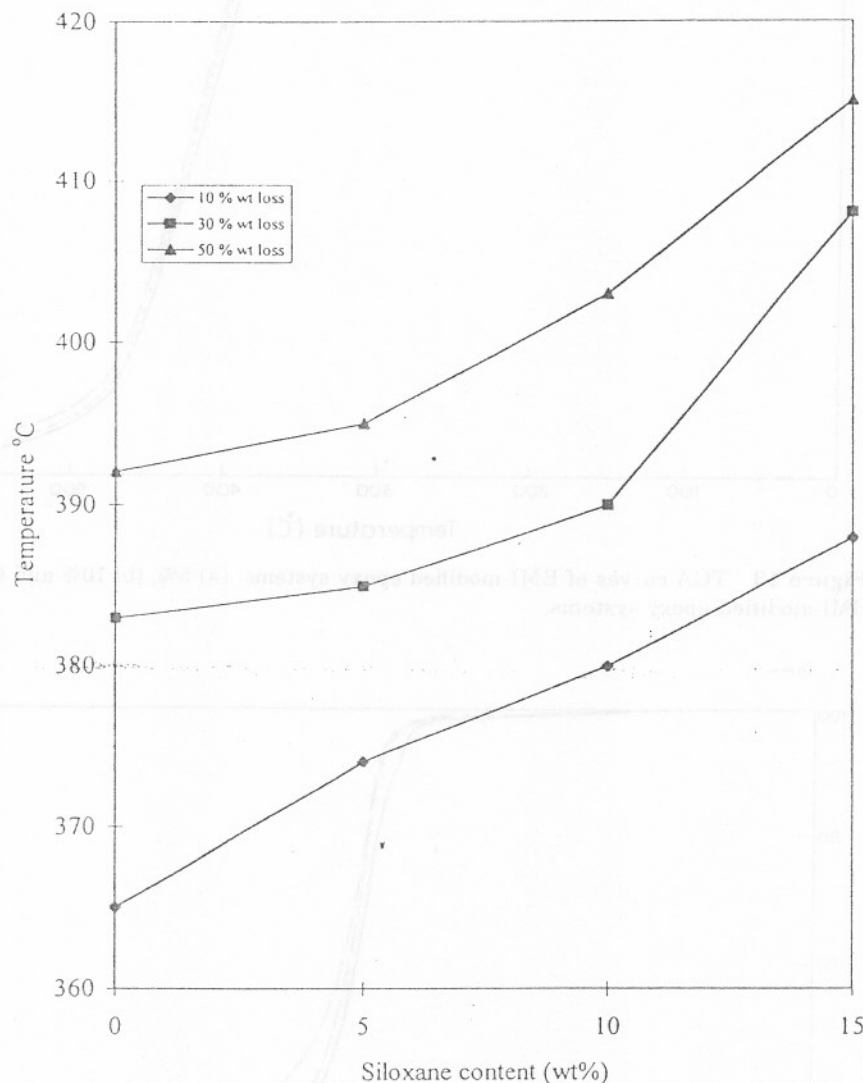


Figure 12 Effect of siloxane content on percentage weight loss.

tween the oxirane ring and the double bond of BMI. The slight increase in the peak maximum temperature with increasing BMI concentration confirms the observation made by Musto et al.<sup>22</sup>

#### Glass Transition Temperature

The glass transition temperatures of the matrix systems are presented in Table II. The glass transition temperature obtained for the epoxy-DDM system is 165°C. Incorporation of HTPDMS into the epoxy resin had no significant effect on the  $T_g$  (Table II and Fig. 8). However, a slight decreasing trend is observed with increasing HTPDMS concentration. The  $T_g$  for 5, 10, and 15% HTPDMS-modified systems are 163, 162, and 160°C, respec-

tively. By the incorporation of BMI into both epoxy and siliconized epoxy systems, the value of the  $T_g$  increases with increasing BMI concentration (Figs. 9 and 10). The increase in the values of  $T_g$  for both BMI-modified epoxy and BMI-modified siliconized epoxy systems are due to homopolymerization of BMI rather than Michael addition. Michael addition reaction leads to the formation of thermally weak amine linkage and ultimately reduces the crosslinking density due to chain extension,<sup>26</sup> whereas BMI homopolymerization leads to the thermally stable C—C linkage. The increase in  $T_g$  confirms that the BMI homopolymerization reaction is predominant over Michael addition. Further, it lends support to the

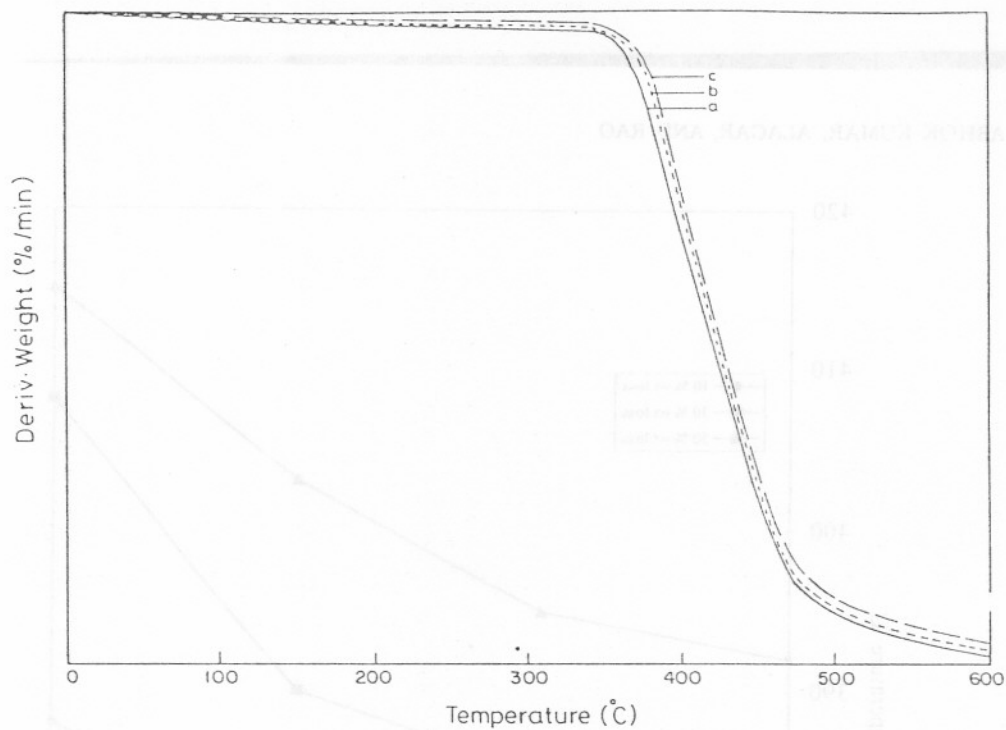


Figure 13 TGA curves of BMI-modified epoxy systems: (a) 5%, (b) 10% and (c) 15% BMI-modified epoxy systems.

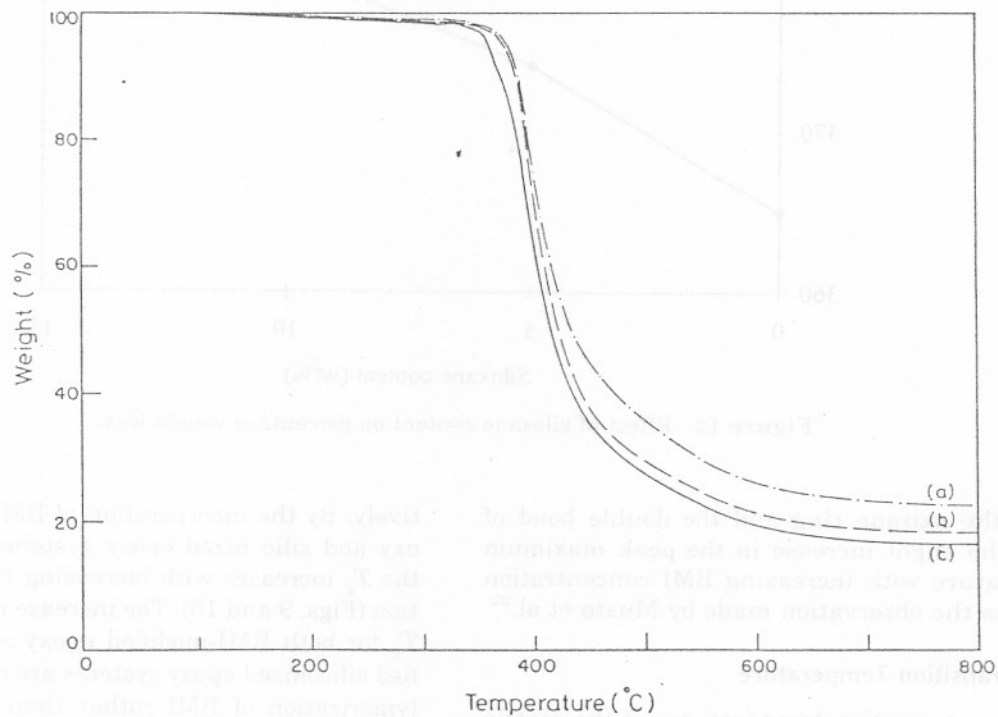


Figure 14 TGA curves of 10% siliconized epoxy/BMI systems: (a) 5%, (b) 10%, and (c) 15% BMI modified 10% siliconized epoxy systems.



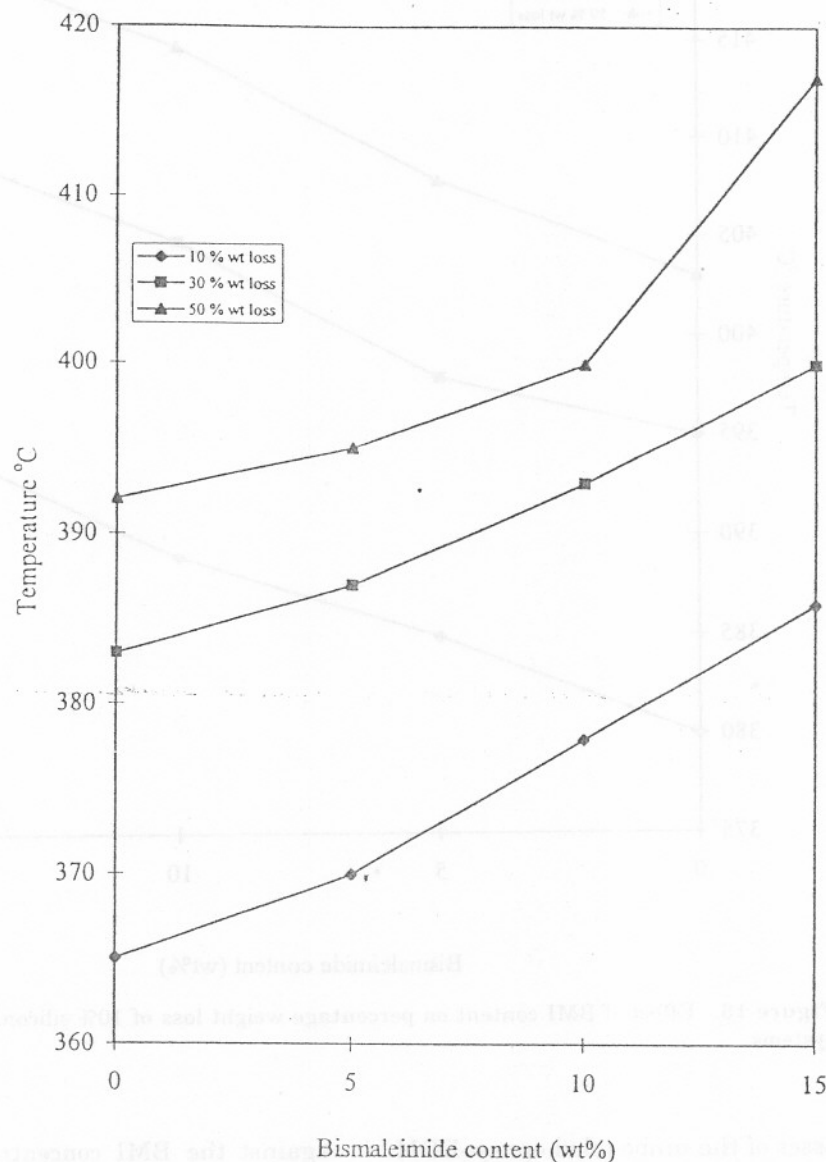


Figure 15 Effect of BMI content on percentage weight loss.

earlier observation made by Musto et al. that, in the presence of epoxy resin, the BMI homopolymerization reaction starts even at 120–140°C.<sup>22</sup> The single  $T_g$  value obtained for the BMI-modified systems (Figs. 9 and 10 and Table II) further confirms the presence of intercrosslinked network structure.

#### Thermogravimetric Analysis

Thermogravimetry is the most important method to assess the thermal stability of polymeric materials. Incorporation of siloxane into epoxy resin

improves the thermal stability and enhances the degradation temperature according to its percentage concentration (Fig. 11). The presence of the siloxane skeleton in the system delays the degradation and a high amount of thermal energy is required to attain the same weight loss when compared with that of an unmodified epoxy system. The delay in degradation by the siloxane moiety may be attributed to the stability of the inorganic nature of the siloxane structure, which may stabilize the epoxy resin from the heat. For example, the temperature required for 10, 30, and

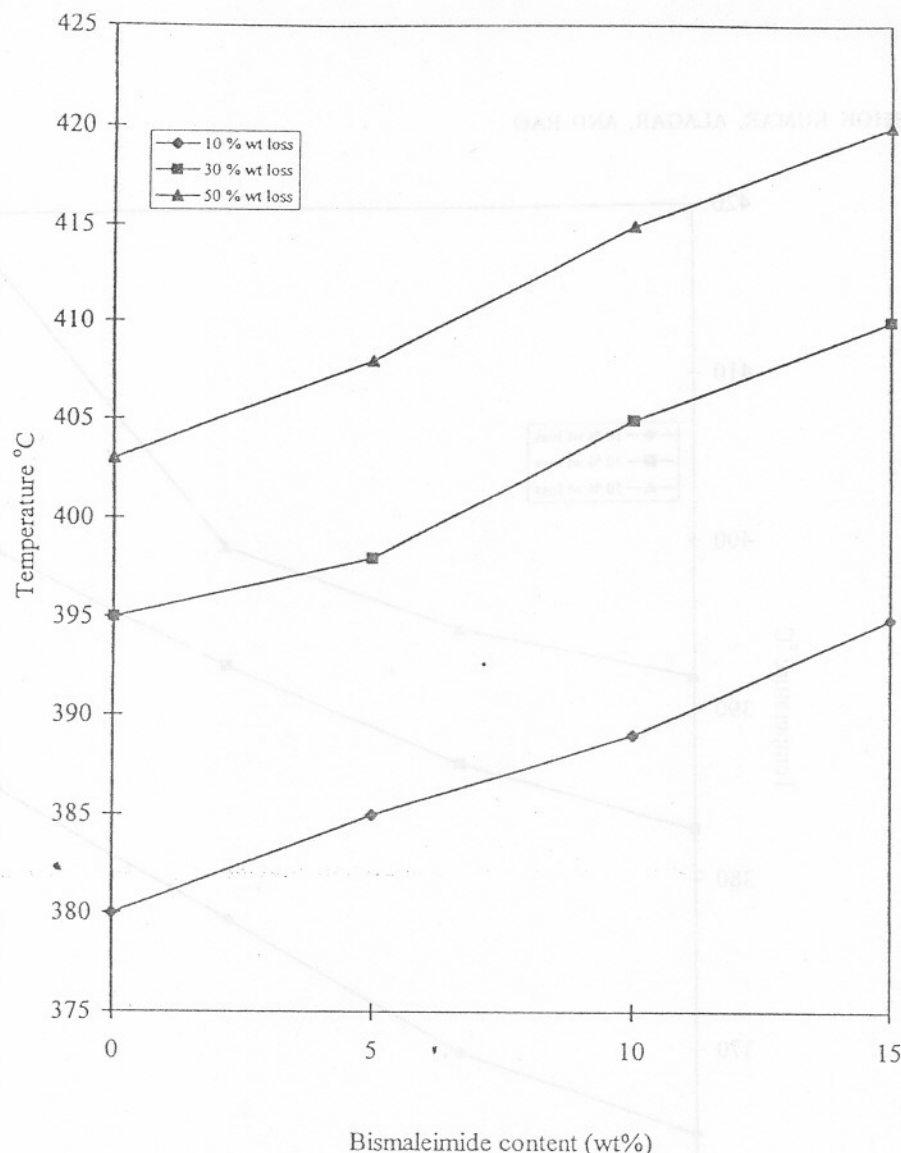
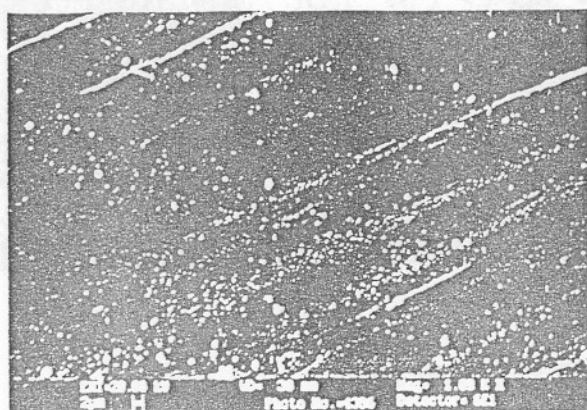


Figure 16 Effect of BMI content on percentage weight loss of 10% siliconized epoxy systems.

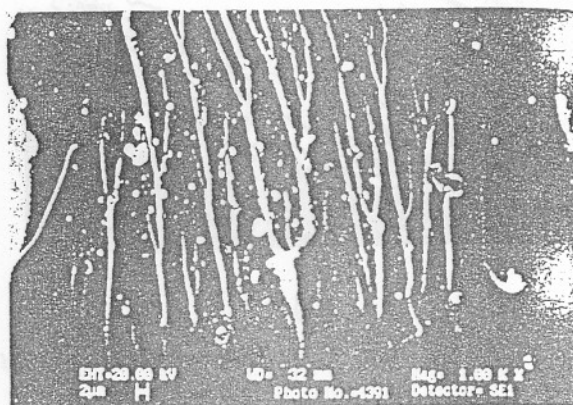
50% weight losses of the unmodified epoxy-DDM system are 365, 383, and 392°C, whereas the temperatures required to attain the same weight losses for the 15% HTPDMS-modified system increased to 388, 408, and 415°C, respectively (Fig. 12). A similar trend is observed for 5 and 10% HTPDMS-modified epoxy systems.

From Figures 13 and 14, it is observed that the thermal degradation temperature of both BMI-modified epoxy and BMI-modified siliconized epoxy systems increases with increasing BMI content. The plot of the degradation temperature

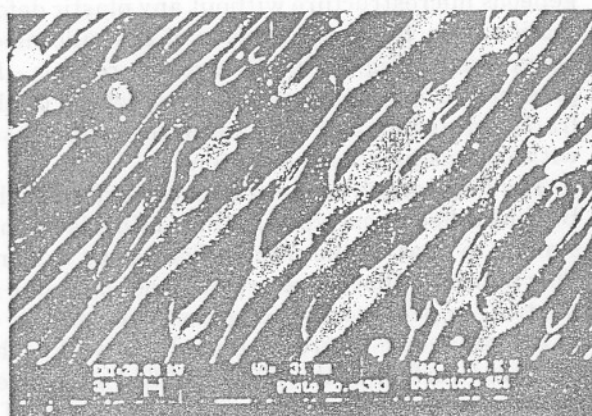
against the BMI concentration is presented in Figure 15. From Figure 15, it is evident that the degradation temperature increases with increasing BMI concentration as observed in the case of HTPDMS-modified systems. The delay in degradation is mainly due to the thermally stable aromatic-heterocyclic structure of BMI and the formation of intercrosslinking network with epoxy resin. The thermal stability of the BMI-modified siliconized epoxy system is slightly higher than that of the BMI-modified epoxy and HTPDMS-modified epoxy systems (Fig. 16). For



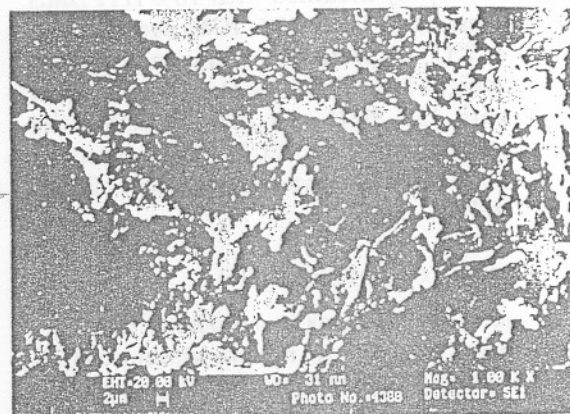
(a)



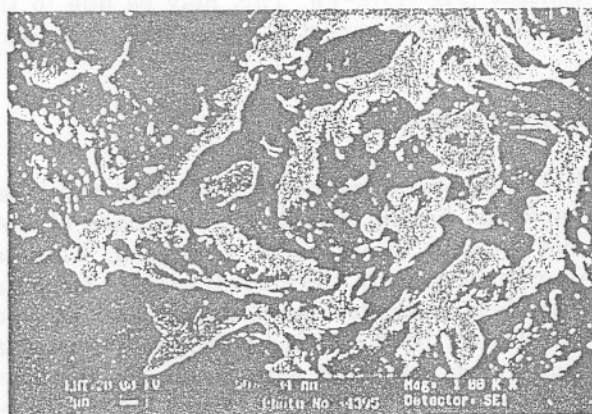
(b)



(c)



(d)



(e)

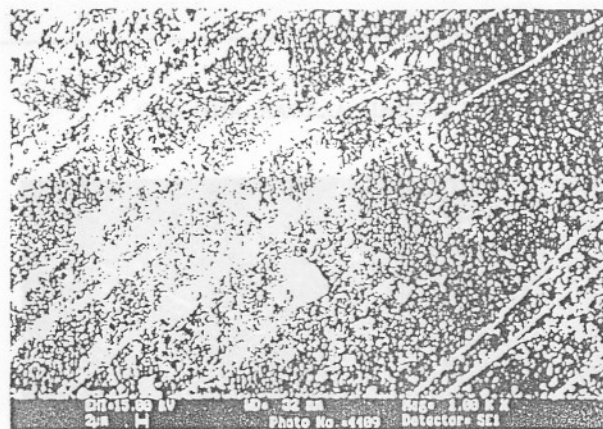


(f)

**Figure 17** SEM micrographs of fracture surfaces of (a) unmodified epoxy, (b) 5%, (c) 10%, and (d) 15% siloxane-modified epoxy; (e) 5%, (f) 10%, and (g) 15% BMI-modified 10% siliconized epoxy, and (h) 10% BMI-modified epoxy systems.



(g)



(h)

Figure 17 (Continued from the previous page)

example, the temperature required for a 50% weight loss of epoxy modified with 15% HTPDMS and epoxy modified with 15% BMI systems are 415 and 417°C, respectively, whereas to attain the same weight loss (50%) for the epoxy system modified with 15% BMI and 10% HTPDMS the temperature increases to 420°C. This enhancement is due mainly to a synergistic effect of BMI and HTPDMS.

#### Heat-distortion Temperature (HDT)

HDT is one of the methods to determine the thermomechanical behavior of matrix systems. HDT values for epoxy, HTPDMS-modified epoxy, BMI-modified epoxy, and BMI-modified siliconized epoxy systems are presented in Table II. From Table II, it is evident that HDT decreases with increasing HTPDMS concentration. This may be explained as due to the presence of the flexible  $-\text{Si}-\text{O}-\text{Si}-$  linkage. However, HDT increases for epoxy and siliconized epoxy modified with BMI systems according to its percentage incorporation. The enhancement in the values of HDT for BMI-modified systems is due to the high crosslinking and heterocyclic-aromatic structure imparted by BMI.

#### Microscopy Investigation

The SEM was used to investigate the morphology of unmodified epoxy, siliconized epoxy, BMI-modified epoxy, and BMI-modified siliconized epoxy systems (Fig. 17). The SEM micrograph of the fractured surface of the unmodified epoxy system

[Fig. 17(a)] reveals a smooth, glassy, and homogeneous microstructure without any plastic deformation. The fractured surface of the siliconized epoxy resin [Fig. 17(b-d)] system reveals the presence of a heterogeneous morphology of the fractured surface and the heterogeneity increases with increasing siloxane content.

The micrograph of the fractured surface of the BMI-modified epoxy system [Fig. 17(h)] is almost similar to that of the unmodified epoxy system. This indicates that there are no phase domains of the two components and suggests the formation of a homogeneous intercrosslinked network. The fractured surface of the BMI-modified siliconized epoxy system, however, reveals the presence of a heterogeneous morphology and also a smooth fracture surface is observed with increasing BMI content [Fig. 17(e-g)]. This may be due to the brittle behavior imparted by the BMI skeleton.

#### CONCLUSIONS

BMI-modified siliconized epoxy intercrosslinked networks, having varied concentrations of BMI and siloxane units, were developed. Thermal properties, namely, the glass transition temperature, heat-distortion temperature, and thermal stability, of BMI-modified siliconized epoxy matrices were compared with those of unmodified epoxy systems, siliconized epoxy systems, and BMI-modified epoxy systems. HTPDMS modification imparts higher thermal stability to the epoxy systems without significantly improving the glass



transition and heat-distortion temperatures. However, BMI-modified siliconized epoxy systems exhibit intermediate behavior between the above two extremes, in addition to improvement in toughness behavior, which is the prime objective of epoxy modification with flexible siloxane units and rigid BMI units.

Further, the single glass transition values obtained for the siliconized epoxy systems and BMI-modified siliconized epoxy systems indicate the presence of an intercrosslinking network. The morphology from the SEM micrograph indicates that the silicone modification gives a distinct heterogeneous morphology, whereas BMI modification has a homogeneous morphology.

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